

**UTILIZATION OF SULFUR DIOXIDE AND
SULFUR TRIOXIDE
TREATMENT OF ORES**

WARREN EDGAR WINSCHÉ

**B.Ch.E., Polytechnic Institute of Brooklyn, 1939
M.S., University of Rochester, 1940**

**AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
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INTRODUCTION

Mixtures of inorganic salts like ferric chloride, zinc chloride, aluminum chloride, eac., with sodium chloride form low melting, conducting liquid systems. These fused systems should be reaction media for many of the inorganic reactions. The purpose of this investigation was to study the reaction of sulfur dioxide and air with inorganic materials suspended or dissolved in fused salt mixtures.

The investigation included: the reaction with ferric oxide suspended in fused sodium chloride-ferric chloride, the reaction with ilmenite suspended in fused sodium chloride-ferric chloride, the reaction with zinc oxide suspended in fused sodium chloride-zinc chloride, and the reaction with sodium chloride in fused sodium chloride-sodium sulfate.

EXPERIMENTAL

The experimental procedure was identical for all the reactions investigated. A mixture of known amounts of the metal chloride and sodium chloride was prepared, fused, and heated to the desired reaction temperature. A weighed amount of the metal oxide was added and a gas stream of sulfur dioxide and air was bubbled through the melt. The agitation produced by the gas bubbles was sufficient to maintain the metal oxide in suspension.

The rate of reaction was determined from the composition of the inlet and exit gas for the reaction of ferric oxide. In the case of ilmenite, zinc oxide, and sodium chloride the extent of reaction was determined by analysis of the melt after the gas flow has been maintained for a definite time interval. The usual procedures were used in analysing the gas streams or residual melts.

RESULTS AND DISCUSSION

(A) The Reaction of Sulfur Dioxide and Air with Ferric Oxide Suspended in Fused Sodium Chloride-Ferric Chloride

The data show that sulfur dioxide and oxygen react with ferric oxide suspended in fused sodium chloride-ferric chloride in the molecular ratio of 2 to 1 to form an insoluble ferric sulfate compound. The rate of reaction is governed by two resistances: the mass transfer resistance for sulfur dioxide from the gas to the reaction zone, and the chemical resistance for a reaction which is first order with respect to the concentration of dissolved sulfur dioxide and approximately second order with respect to the amount of ferric oxide in suspension. The appropriate equation for instantaneous conditions is

$$-\frac{dG}{dt} = \frac{(p_g)_{l.m.}}{\frac{3}{K_{ga}} + \frac{1}{k_{rc}G^2}}$$

where G is the milligram moles of ferric oxide suspended in the melt at time equal to t minutes, K_{ga} is the diffusional coefficient for sulfur dioxide, k_{rc} is the product of the specific reaction rate and Henry's Law constant for sulfur dioxide in the fused melt, and $(p_g)_{l.m.}$ is the logarithmic mean of the partial pressures in atmospheres of the sulfur dioxide in the inlet and exit gases. At 450° K_{ga} is approximately 30 and k_{rc} is approximately 20.

(B) The Reaction of Sulfur Dioxide and Air with Ilmenite Suspended in Fused Sodium Chloride-Ferric Chloride.

The data show that the gases preferentially attack the iron constituent of ilmenite. The extent of reaction was appreciable at 550°C . At 620°C , the iron content was reduced from 25.6% iron to 4.5% iron in one hour of treatment. The major portion of the titanium-enriched ilmenite was recovered in the same particle size range as the original charge. A small amount of finely divided titanium dioxide was formed during reaction.

(C) The Reaction of Sulfur Dioxide and Air with Zinc Oxide Suspended in Fused Sodium Chloride-Zinc Chloride.

The data show that the reaction was negligibly small at 420° and 530°C.

(D) The Reaction of Sulfur Dioxide and Air with Sodium Chloride in Fused Sodium Chloride-Sodium Sulfate.

The data show that the rate of reaction was negligibly small at 700°C. Increased intimacy of liquid-gas contact did not have a beneficial effect. Rutile suspended in the fused medium was not a catalyst for reaction.

CONCLUSIONS

Sulfur dioxide and air react with some metal oxides suspended in a fused salt system. The overall resistance to the reaction may be a combination of both a physical and a chemical resistance. In the case of mixed oxides the gas may exert a preferential attack upon one of the oxide constituents.

PRACTICAL CONSIDERATIONS

This investigation has shown that fused salt systems are reaction media for some inorganic reactions. From the practical point of view this is of no interest unless the product of reaction can be recovered. One case in which no difficulty in product recovery would arise is a reaction in which the products are gaseous at the reaction temperature.

This suggests the use of fused salts as catalysts for inorganic and organic gas reactions. The fused salts would possess several unique advantages over the usual solid or solid supported catalysts. Their relatively high specific heats would give excellent temperature control in reactions that are highly endo- or exothermic. Their lack of a permanent surface should make them resistant to the type of poisoning usually associated with the deterioration of the surface in solid catalysts. Other advantages could be suggested for specific reactions.

VITA

The author was born on January 26, 1917, in Brooklyn, New York. After being graduated from the Erasmus Hall High School in Brooklyn in 1935, he entered the Polytechnic Institute of Brooklyn, and in 1939 was granted the degree of Bachelor of Chemical Engineering. He entered the Graduate School of the University of Rochester in 1939 and held a teaching assistantship in chemical engineering. He was granted the degree of Master of Science in 1940.

In September, 1940, he entered the Graduate School of the University of Illinois. From that date to June, 1942, he held the Grasselli Research Fellowship in chemical engineering. From September, 1942, to date he has held a University Fellowship in chemistry.

He is a member of Sigma Xi, Phi Lambda Upsilon, the American Chemical Society, and the American Institute of Chemical Engineers.

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H. F. Johnstone, H. C. Weingartner, and Warren E. Winsche, The System Ferric Chloride-Sodium Chloride, **J. Amer. Chem. Soc.**, **64**, 241(1942)



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